

# Nucleation, solvation and boiling of helium excimer clusters

<sup>1</sup>Luis G. Mendoza Luna, <sup>1</sup>Nagham M. Siltagh, <sup>1</sup>Mark J. Watkins,

<sup>2</sup>Nelly Bonifaci, <sup>2</sup>Frédéric Aitken, <sup>1</sup>Klaus von Haeften\*

<sup>1</sup>*University of Leicester, Department of Physics & Astronomy, Leicester, LE1 7RH, United Kingdom and*

<sup>2</sup>*G2ELab-CNRS, Equipe MDE 25, Av. des Martyrs, BP 166, 38042 Grenoble Cedex 9, France*

(Dated: December 8, 2015)

Helium excimers generated by a corona discharge were investigated in the gas and normal liquid phases of helium as a function of temperature and pressure between 3.8 and 5.0 K and 0.2 and 5.6 bar. Intense fluorescence in the visible region showed the rotationally resolved  $d^3\Sigma_u^+ \rightarrow b^3\Pi_g$  transition of  $\text{He}_2^*$ . With increasing pressure, the rotational lines merged into single features. The observed pressure dependence of linewidths, shapes and lineshifts established phases of coexistence and separation of excimer-helium mixtures, providing detailed insight into nucleation, solvation and boiling of  $\text{He}_2^*\text{-He}_n$  clusters.

PACS numbers: Valid PACS appear here

The ability to resolve rotational lines at low temperatures provides exceptional sensitivity for investigating molecule-solvent interactions. For example, infrared spectra of molecules embedded in 0.4 K cold  $^4\text{He}$  droplets [1] display sharp, discrete lines, indicating both free rotation and the superfluidity of the  $^4\text{He}$  droplets [2]. A decreased B-constant and a degree of line broadening reflect an interaction of the molecule with the normal component of helium at the interface [3, 4] with the otherwise superfluid helium. Mixed  $^3\text{He}$ - $^4\text{He}$  droplets with more than 60  $^4\text{He}$  atoms are also superfluid and have an even lower temperature of only 0.15 K. Remarkably, in this ultracold environment the linewidth of the rotational features is three times [2] *smaller* than in *pure*  $^4\text{He}$  droplets [5, 6].

In view of these exciting features and distinct temperature effects, this would seem a very promising starting point from which to perform rotationally resolved spectroscopy with control over a wide range of temperatures, beyond 0.15 and 0.4 K, particularly where additional control over pressure might also be possible. While this control is difficult to accomplish in helium droplets in free beams, it is quite readily possible using bulk helium. However, embedding single foreign molecules directly into bulk helium is challenging because at the temperatures of liquid helium all other substances are themselves frozen, [7] and sophisticated techniques are required to achieve this [8–10]. Short-lived helium excimers ( $\text{He}_2^*$ ) as single-molecule probes represent an alternative means of investigation; they have been used both recently [11–16] and in the past to probe the bulk phases of helium by imaging [17] and spectroscopy. Dennis et al. have bombarded 1.7 K cold superfluid helium with electrons and observed fluorescence in the visible spectral range, which originated from transitions between various electronically excited singlet and triplet states of  $\text{He}_2^*$  [18]. Despite an environment of superfluid helium, the spectra did not show discrete rotational lines but rather features that resembled the rotational enve-

lope of P, Q and R transitions. However, in a similar experiment, Hill, Heybey and Walter observed discrete rotational lines in the transient absorption spectrum of  $\text{He}_2^*$  [19] of 1.7 K cold superfluid helium. These lines were shifted from their associated emission-in-helium and gas phase values, though changes in the effective moment of inertia were not reported. Li et al. excited normal-liquid helium with a corona discharge and observed the fluorescent emission of  $\text{He}_2^*$ , similar to Dennis et al., but in this instance sharp, discrete lines were observed [20]. In all these experiments, however, the effects of temperature and the pressure have not been addressed.

To resolve this apparent contradiction and to advance the understanding of solvation in liquids we have recorded fluorescence spectra of  $\text{He}_2^*$  over a wide range of hydrostatic pressures between 0.2 and 5.6 bar, and at temperatures between 3.8 and 5.0 K, covering the gas and normal liquid phases of helium. A corona discharge was chosen for electronic excitation because it can operate over a very wide range of pressures. At low pressures, spectra were observed showing discrete rotational lines. Upon increasing the pressure, the lines broadened and ultimately merged into broad features; the lines were also shifted in frequency. Analysis of the pressure dependence of this line shift revealed that  $\text{He}_2^*$  excimers exist in locally heated ‘gas pockets’ as well as in solvated states, both of which contribute to the associated spectrum. Simulations of the gas phase spectrum show that about 20% of the molecules are in a solvated state, regardless of pressure and temperature. At 3.8 K, features of solvated  $\text{He}_2^*$  appear at pressures slightly lower than the saturated vapour pressure (SVP) of *pure* helium, indicating that clusters of excimers and ground state helium atoms form at conditions where helium is not yet in the liquid state. The points of cluster formation, indicating the SVP curve of the mixed phase of  $\text{He}_2$  and He, were found to cross the SVP curve of *pure* helium at higher temperatures. Consequently, the mixed  $\text{He}_2\text{-He}$  system boils in this region before *pure* helium, giving rise to the

formation of localised ‘gas pockets’.

The experimental setup was conceptually similar to that described by Li et al. [20], but employed a closed-cycle Oxford Instruments Heliox AC-V He3 cryostat. A micro-discharge cell, with an internal volume of 4 ml and made of oxygen-free copper (OFHC), was attached to the  $^3\text{He}$  stage, but it was found that sufficient cooling power could only be provided after bridging the second stage with copper strips. With these bridges, the cell could reach a minimum temperature of 3.2 K, which was measured by a calibrated Cernox resistor within  $\pm 3$  mK [21]. The cell was equipped with electrodes in a point-plane configuration, the 250 nm-radius tip having been etched from a tungsten wire, with an electrode gap of 3 to 4 mm. After purging and evacuating the lines with a scroll pump, up to 100 bar helium of N6.0 research grade purity was introduced via stainless steel pipes. A discharge was ignited using a Spellman high voltage power supply using negative voltages between 3 and 10 kV connected to the tip electrode, and currents between 0.1 and 10  $\mu\text{A}$  depending on the thermodynamic phase of the helium. Fluorescence emitted from the discharge region was collected by an achromatic lens, which also served as a high pressure window of the cell to maximise detection efficiency. The fluorescence light was collimated by two further lenses and then guided, via two adjustable, metal-coated mirrors and an  $f = 150$  mm achromatic lens, onto the entrance slit of an Andor Technology Shamrock SR303i Czerny Turner spectrometer equipped with a Peltier-cooled ( $-65^\circ\text{C}$ ) CCD camera (Andor iDus DV420, CCD-12855). A 1200  $\text{mm}^{-1}$  grating blazed at 500 nm was employed, centred around 640 nm, and high resolution spectra were recorded (at a resolution of 0.2 nm).

Fluorescence spectra at 3.8, 4.0 and 5.0 K showing the  $d^3\Sigma_u^+ \rightarrow b^3\Pi_g$  transition of  $\text{He}_2^*$  in the  $n = 3$  Rydberg state [22] are shown in figure 1 for different hydrostatic pressures, covering both the gas and the liquid phase of helium. A glow discharge spectrum recorded in the evacuated cell is shown as reference for both vacuum line positions [22] and the spectrometer’s resolution. P and R lines are resolved; the Q lines lie almost on top of each other and are thus too closely spaced to be resolved with our spectrometer. All lines are split into groups of six energetically close transitions due to spin-spin and spin-orbit interactions of the triplet levels in Hund’s case (b) [23]. The triplet splitting also cannot be resolved at our resolution.

At low cell pressures, sharp, discrete lines are observed. With increasing pressure, the lines shift in frequency, broaden and change their shape, particularly the P(2) and Q lines. By comparison with the glow discharge spectrum, it can be clearly seen that the P(2) line quickly gains intensity compared to the other P lines. Also, the P(2) line merges at a certain, distinct pressure - for each given isotherm - with the Q-branch. At 3.8 K this happens between 0.2 and 0.6 bar, at 4.0 K between 0.7 and

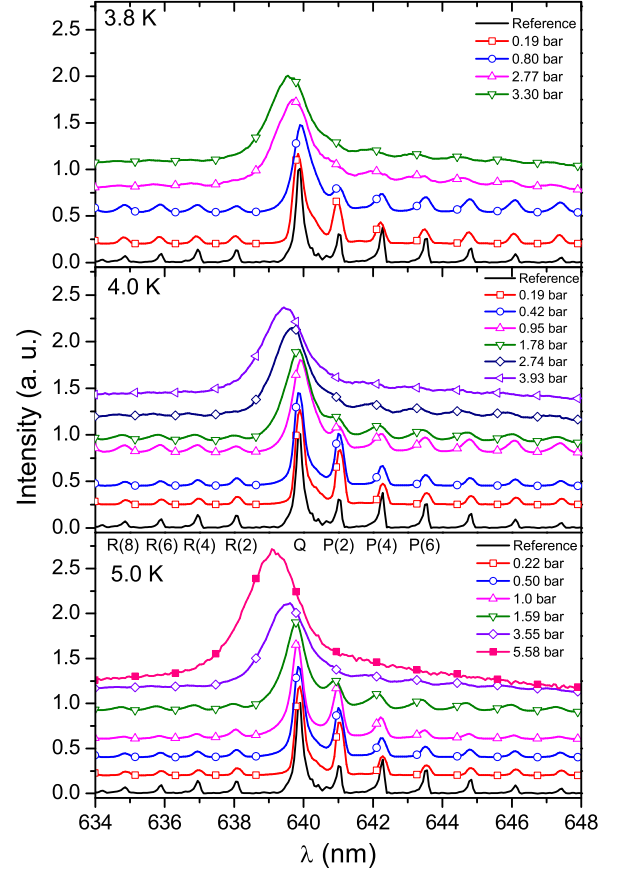


FIG. 1. Spectra of  $\text{He}_2^*$  in helium as a function of pressure for three isotherms. The lines of a glow discharge reference spectrum are labelled R, Q, P as a function of quantum number  $N$  (Hund’s case (b)). With increasing pressure, the lines broaden and shift. Note also that with increasing pressure the Q and P(2) lines gain more intensity compared to other lines, and ultimately merge. Intensities and offset have been scaled for better visualisation.

0.9 bar, and at 5.0 K between 1.6 and 3.6 bar. Rotational resolution vanishes when pressures increase much beyond the SVP of *pure* helium, first for R-lines and then for P lines.

To analyse the changes in linewidth and line position, the lines were separately fitted with Lorentzian functions. Over a large range of pressures the lines remain symmetric, hence the fits with Lorentzians represent a good way to assess and quantify line broadening by using the spectral width as the sole parameter. To account for the convolution of the widths of the Lorentzian lines with the spectrometer response, 0.2 nm was subtracted from the fitted values, which is the instrument resolution derived from the glow discharge spectrum.

Figure 2 shows the linewidths obtained from the fitting procedure as a function of pressure; Q lines are found to broaden more rapidly than P lines. At 3.8 and 4.0 K,

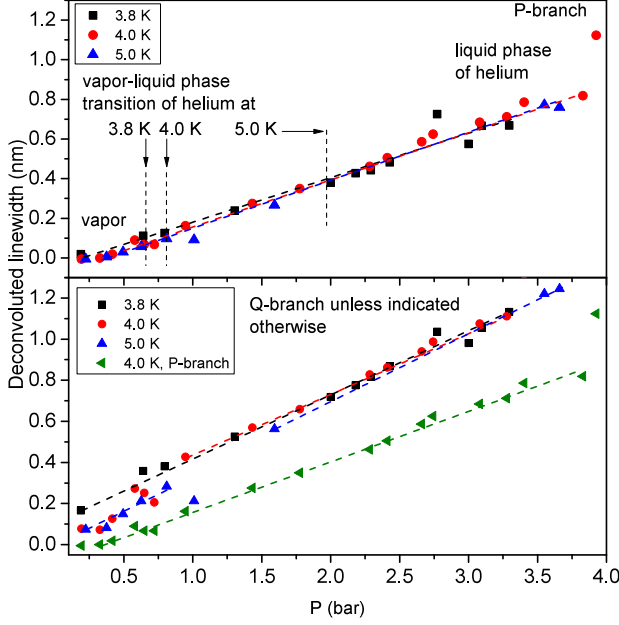


FIG. 2. Pressure dependence of the linewidth of  $\text{He}_2^*$  features (after deconvolution, see text) for 3.8, 4.0 and 5.0 K isotherms. Upper panel: analysis of P-lines. Lower panel: features in the region of the Q-transitions of  $\text{He}_2^*$ . The dashed lines show trend lines. Results for P-transitions are shown for comparison. The line broadening of the 'Q-transitions' with pressure is larger than for the P-lines.

the linewidth increases linearly with pressure. Potential differences between the gas phase and the liquid phase of helium are too small to be resolved.

Figure 3 shows the Q- and P-lineshifts,  $\Delta\lambda(p)$ , as a function of pressure. The lineshifts can be grouped into different pressure regions: at 3.8 and 4.0 K and pressures below the SVP of liquid helium, the Q-lines show small, and only slightly increasing shifts when the pressure is increased. The Q-lines then exhibit a small, but abrupt red shift. Further increases of pressure then result in linearly, and more greatly increasing, blue-shifts than for lower pressures. The observed abrupt change indicates a change in the structure of the perturbing environment and is attributed to the formation of a dense solvation shell. Lineshift coefficients,  $\frac{\partial\Delta\lambda}{\partial p}$  and  $\Delta\lambda_0$ , were obtained for the gas and solvated phases separately by fitting the function  $\Delta\lambda(p) = \frac{\partial\Delta\lambda}{\partial p}p + \Delta\lambda_0$  to the data and are shown in table I, with the exception of the 3.8 K isotherm where at pressures before the red shift, only one data point is available. At 4.0 K, the gas-phase lineshift coefficient is 0.03 nm/bar, distinctly lower than the 0.17 nm/bar found for the condensed phase.

Overall, the P-lines also show a linearly increasing blue shift. At 4.0 K, the lineshift coefficient increases from 0.085 nm/bar to 0.128 nm/bar after the SVP is crossed – a change that is smaller than that observed for the Q

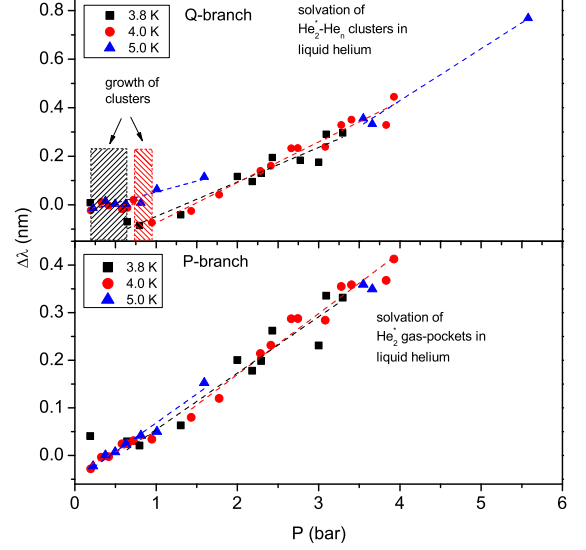


FIG. 3. Line-shifts as obtained through fitting with Lorentzians. Upper panel: 'Q-transitions'. Lower panel: P-transitions. For the 3.8 and 4.0 K isotherms the line-shifts differ greatly between Q and P transitions; Q-features show larger line shifts with pressure than P-lines. Also, abrupt changes (red shifts) indicating phase transitions are observed.

lines (see table I).

These observations indicate that the P and Q features must originate from different species because in molecular spectra the positions of P and Q lines are mutually dependent, as defined by the appropriate rotational constants (and hence, structure). We will see below that our observations can be readily explained by a superposition of spectra from excimers in two different types of environments:  $\text{He}_2^*$  residing (i) in a solvated state and (ii) in hot gas pockets. Both species contribute, with different spectral weights, to the Q and P lines of the spectrum. These different contributions are apparent in the significantly larger intensities of the Q and P(2) features compared to the P and R lines of higher N in figure 1. For solvated, and hence cold,  $\text{He}_2^*$ , only the lowest allowed quantum state,  $N = 1$ , will be populated because the next higher

TABLE I. Line shift coefficients in the gas phase and liquid regions.

T			slope, $\frac{\partial\Delta\lambda}{\partial p}$ [nm/bar]	intercept, $\Delta\lambda_0$ [nm]
4.0 K	(Q)	gas	$0.03 \pm 0.04$	$-0.01 \pm 0.03$
4.0 K	(P)	gas	$0.09 \pm 0.01$	$-0.03 \pm 0.03$
5.0 K	(Q)	gas	$0.07 \pm 0.02$	$-0.03 \pm 0.09$
3.8 K	(Q)	liq.	$0.14 \pm 0.01$	$-0.19 \pm 0.03$
4.0 K	(Q)	liq.	$0.17 \pm 0.01$	$-0.24 \pm 0.03$
4.0 K	(P)	liq.	$0.13 \pm 0.01$	$-0.09 \pm 0.03$
5.0 K	(Q)	liq.	$0.11 \pm 0.02$	$-0.07 \pm 0.09$

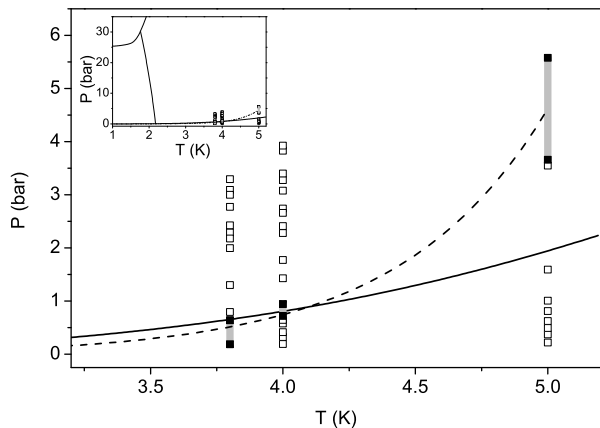


FIG. 4. Phase diagram of normal liquid helium. The squares indicate measured data points on the 3.8, 4.0 K and 5.0 K isotherms. The filled squares confine the region where the phase transitions of the  $\text{He}_2^*$ -He system were observed; the dashed line is an exponential fit to the mid-points. Inset: overview section of helium phase diagram with solid, liquid, superfluid, gas and supercritical phases.

allowed level,  $N = 3$ , is separated from it by  $75 \text{ cm}^{-1}$ . The only transitions emerging from the  $N = 1$  state are the Q(1) and P(2) lines.

To disentangle the two contributions we have simulated the gas phase spectrum and subtracted it from the measured features. The simulation accounted for the triplet splitting of rotational levels, Boltzmann and Hönl-London factors and line broadening using a convolution of the lines with a Lorentzian function. Figure 5 illustrates this procedure for 2.0, 2.8 and 3.3 bar at 3.8 K. Best fits with the sharp line component were obtained for a rotational temperature of 750 K and for higher hydrostatic pressures. Significant intensity of the difference spectrum in the regions of the P-lines shows that the assumed Boltzmann distribution is only approximate and that the excimers are not strictly in equilibrium with a thermal bath at 750 K. A temperature three orders of magnitude higher than the solvent nevertheless indicates inefficient energy exchange with the bulk helium environment, similar to excimers ejected from electronically excited helium droplets [24, 25] and excimers residing on the surface of helium droplets [26, 27]. The B-constants varied very little, and always lay within 10% the associated excimer gas phase values.

The difference spectrum revealed 20% of the total intensity in the region of the Q-transitions, with no rotational line structure, suggesting that molecular rotation is strongly hindered, essentially as one would expect in normal liquid helium [5, 6]. Supported by the resemblance to the spectrum of OCS in normal liquid  $^3\text{He}$ , [6] we tentatively attribute the difference spectrum to the envelope of a spectrum composed of the P(2) and Q(1)

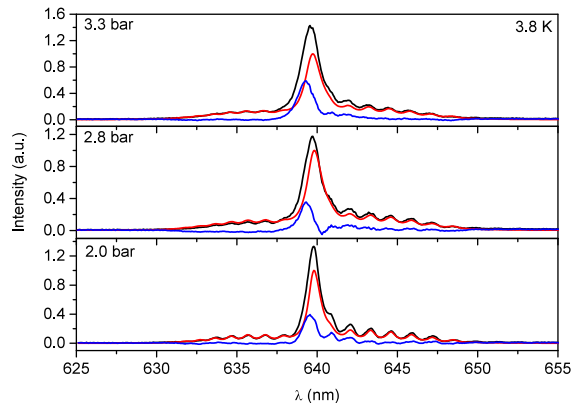


FIG. 5. Illustration of how difference spectra were derived from a simulated spectrum. The black line represents the measured spectrum; the red and the blue lines represent the simulated and difference spectra, respectively. The difference spectra show features in the region of the Q-transitions that are offset to shorter wavelength, explaining how the contribution from solvated excimers produces additional blue-shifting in only this region.

lines of  $\text{He}_2^*$ .

Summarising, our analysis of line broadening and lineshifts provides evidence for  $\text{He}_2^*$  residing in three different environments: (i) in the gas phase, (ii) solvated and thermalised in clusters or liquid helium, and (iii) in hot gas pockets within liquid helium. All three states show different lineshift coefficients, the 'gas pocket' coefficient lying between those of the gas and the condensed phases. The greater sensitivity to pressure changes means that the perturbation of the  $\text{He}_2^*$  in the gas pockets is larger than that in the gas phase, indicating that the particle density inside the pockets is rather high or, equivalently, the size of the pockets is rather small, presumably only a little larger than the  $n = 3$  Rydberg-'bubble' diameter of  $15 \text{ Å}$  [28].

The observed discontinuities in the pressure-dependence of the lineshifts can be readily explained as phase transitions of a mixed phase of  $\text{He}_2^*$  excimers and ground state helium atoms. We have marked the position of these discontinuities in the phase diagram of helium in Figure 4. At 3.8 K this happens slightly below the SVP curve of *pure* helium, whilst at 4.0 K this happens *on* the *pure* helium SVP curve, whilst at 5.0 K this happens slightly above. These results suggest an SVP curve for the  $\text{He}_2^*$ -He system which intersects the SVP curve of *pure* helium at 4.0 K.

This has the following implications: below 4.0 K, and in a region bounded by the SVP of *pure* and *mixed* helium, atoms nucleate on  $\text{He}_2^*$  and form clusters. The fact that clusters of  $\text{He}_2^*$  and He form before pure helium condenses means that the  $\text{He}_2^*$ -He potential should have a shallow, long-range minimum for the d state. Such a

minimum has not shown up yet in calculations [28].

Above 4.0 K, and between the SVP curves of *pure* and *mixed* helium,  $\text{He}_2^*$ -He mixtures can exist in gaseous form within liquid helium. These gas bubbles are stable above the SVP of *pure* helium within the liquid phase. This explains why sharp lines were observed in the line spectra produced by corona discharge in normal liquid helium [20]. Furthermore, above 4.0 K, excess energy from the corona discharge excitation leading to local heating can be favourably released into  $\text{He}_2^*$  residing in gas pockets, resulting in  $\text{He}_2^*$  excimers which are then able to boil within their own solvation shell.

$\text{He}_2^*$  reaching the surface of electronically excited helium clusters desorb [24, 25, 29, 30] or remain bound to the surface [26, 27]. Rotationally resolved spectra show that there are no helium atoms attached to the desorbed excimers [24, 25]. Our findings suggest that desorption or surface trapping depend on the temperature. Hence, investigation of the respective transitions can provide insight into heating after electronic excitation.

In conclusion, we have investigated the spectra of  $\text{He}_2^*$  in normal liquid helium as a function of pressure and temperature. At low pressure, rotationally resolved lines were observed. The lines shifted in energy and broadened until they completely vanished as pressure was increased. Analysis of lineshifts and line broadening, and simulations of the  $\text{He}_2^*$  gas phase spectrum, show evidence for the presence of (i) cold excimers solvated in helium, (ii) hot excimers in gas pockets within liquid helium and – when the pressure is low enough – (iii) in the gas phase. The excimers rotate freely in the gas pockets and can thus display high rotational temperatures of 750 K, while the solvated excimers are thermalised and hindered in their rotation. Our work establishes a phase diagram for a mixed phase of  $\text{He}_2^*$  and ground-state helium, explaining the release of energy by formation of microscopic gas bubbles, the desorption of ‘naked’ excimers from electronically excited helium clusters, and the nucleation and stabilisation of  $\text{He}_2^*$ -He<sub>n</sub> at temperatures below 4 K.

KvH and FA acknowledge funding by the British Council through the Alliance Programme. KvH is grateful for financial support through The Leverhulme Trust (Research Grant F00212AH), the Royal Society (International Exchange Grant IE130173) and the Université Joseph Fourier for a Visiting Professorship. LGML acknowledges financial support from the Mexican Consejo Nacional de Ciencia y Tecnología (CONACYT) Scholarship number 310668, ID 215334.

---

\* kvh6@le.ac.uk

- [1] M. Hartmann, R. Miller, J. Toennies, and A. Vilesov, Phys. Rev. Lett. **75**, 1566 (1995)
- [2] J. P. Toennies and A. F. Vilesov, Angew. Chem. Int. Ed. **43**, 2622 (2004)
- [3] Y. Kwon and K. B. Whaley, Phys. Rev. Lett. **83**, 4108 (1999)
- [4] Y. Kwon, P. Huang, M. Patel, D. Blume, and K. Whaley, J. Chem. Phys. **113**, 6469 (2000)
- [5] S. Grebenev, J. Toennies, and A. Vilesov, Science **279**, 2083 (1998)
- [6] B. G. Sartakov, J. P. Toennies, and A. F. Vilesov, J. Chem. Phys. **136**, 134316 (2012)
- [7] V. Kiryukhin, B. Keimer, R. Boltnev, V. Khmelenko, and E. Gordon, Phys. Rev. Lett. **79**, 1774 (1997)
- [8] V. Lebedev, P. Moroshkin, J. Toennies, and A. Weis, J. Chem. Phys. **133**, 154508 (2010)
- [9] V. Khmelenko, S. Mao, A. Meraki, S. Wilde, P. McColligan, A. Pelmenov, R. Boltnev, and D. Lee, Phys. Rev. Lett. **111**, 183002 (2013)
- [10] E. Popov and J. Eloranta, J. Chem. Phys. **142**, 204704 (2015)
- [11] A. Benderskii, R. Zadoyan, N. Schwentner, and V. Apkarian, J. Chem. Phys. **110**, 1542 (1999)
- [12] D. N. McKinsey, W. H. Lippincott, J. A. Nikkel, and W. G. Rellergert, Phys. Rev. Lett. **95**, 111101 (2005)
- [13] W. Rellergert, S. Cahn, A. Garvan, J. Hanson, W. Lippincott, J. Nikkel, and D. McKinsey, Phys. Rev. Lett. **100**, 025301 (2008)
- [14] W. Guo, J. Wright, S. Cahn, J. Nikkel, and D. McKinsey, Phys. Rev. Lett. **102**, 235301 (2009)
- [15] D. Zmeev, F. Pakpour, P. Walmsley, A. Golov, W. Guo, D. McKinsey, G. Ihas, P. McClintock, S. Fisher, and W. Vinen, Phys. Rev. Lett. **110**, 175303 (2013)
- [16] W. Guo, M. La Mantia, D. P. Lathrop, and S. W. Van Sciver, Proc. Nat. Acad. Sci. **111**, 4653 (2014)
- [17] J. Gao, A. Marakov, W. Guo, B. Pawlowski, S. Van Sciver, G. Ihas, D. McKinsey, and W. Vinen, Rev. Sci. Instr. **86**, 093904 (2015)
- [18] W. S. Dennis, J. E. Durbin, W. A. Fitzsimmons, O. Heybey, and G. K. Walters, Phys. Rev. Lett. **23**, 1083 (1969)
- [19] J. Hill, O. Heybey, and G. Walters, Phys. Rev. Lett. **26**, 1213 (1971)
- [20] Z.-L. Li, N. Bonifaci, F. Aitken, A. Denat, K. von Haeften, V. Atrazhev, and V. Shakhmatov, Eur. Phys. J. Appl. Phys. **47** (2009)
- [21] On the SVP, the temperature of the helium inside the cell deviated by no more than 0.1 K on the sensor readout
- [22] M. L. Ginter, J. Mol. Spec. **18**, 321 (1965)
- [23] P. R. Fontana, Phys. Rev. **125**, 220 (1962)
- [24] K. von Haeften, A. R. B. de Castro, M. Joppien, L. Mousavizadeh, R. von Pietrowski, and T. Möller, Phys. Rev. Lett. **78**, 4371 (1997)
- [25] K. von Haeften, T. Laarmann, H. Wabnitz, and T. Möller, Phys. Rev. Lett. **88**, 233401 (2002)
- [26] S. Yurgenson, C.-C. Hu, C. Kim, and J. Northby, Eur. J. Phys. D: At., Mol. Clusters-Atomic, Molecular, Optical and Plasma Phys. **9**, 153 (1999)
- [27] L. G. Mendoza-Luna, M. Watkins, K. von Haeften, N. Bonifaci, and F. Aitken, Eur. J. Phys. D: At., Mol. Clusters **67**, 1 (2013)
- [28] J. Eloranta and A. V. Apkarian, J. Chem. Phys. **115**, 752 (2002)
- [29] K. von Haeften, T. Laarmann, H. Wabnitz, and T. Möller, J. Phys. B, At. Mol. Opt. Phys. **38**, S373 (2005)
- [30] O. Bünermann, O. Kornilov, D. J. Haxton, S. R. Leone, D. M. Neumark, and O. Gessner, J. Chem. Phys. **137**, 214302 (2012)